N-type Porous Silicon Fabricated under Variable Photon flux: Photoluminescence and Raman Studies

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Abstract—

Raman scattering and photoluminescence (PL) measurements on <100> oriented n-type crystalline silicon (c-Si) and porous silicon (PS) samples were carried out. PS samples were prepared by anodic etching of c-Si under the illumination of light for variable photon flux. The Raman peak is almost unshifted for the oxidized nanocrystals with respect to its bulk value but some asymmetry was observed. Raman spectra of porous silicon are fitted by a theoretical model based on quantum confinement of electrons in Si nanocrystallites having spherical and cylindrical forms. This model permits one to correlate the Raman spectra with the PS structure.. It was shown that the crystallite size decreases throughout as photon-flux is increased under laser irradiation in air. The photoluminescence (PL) from PS increased in intensity and blue shifted with increase in laser irradiation intensity. Blue shifting of PL is consistent with quantum confinement of electron in Si nanocrystallites.This experiment shows that fabrication of high efficient photoluminescence devices is possible by further tuning the light illumination level.

Keywords -- Photoluminescence, Porous silicon, Quantum confinement, Raman scattering

I. INTRODUCTION

Crystalline silicon (*c*-Si) is the single most important material of the last century that has been the cornerstone
of the semiconductor industry and has spearheaded extraordinary technological advancements. Bulk *c*-Si, however, has one major deficiency in that it has an indirect bandgap, making it unsuitable for integrating light with electronics (optoelectronics). Thus, *c*-Si has only very poor luminescence in the near infrared (1100 nm) region. As a result of this, solid-state light-emitting diodes (LEDs) are generally fabricated from direct band gap semiconductors such as GaAs, organic compounds and more recently nanostructured materials. These solutions not only make the integration of optoelectronic devices with conventional Si technology difficult but also expensive. It is against this background that the observation of intense visible luminescence in porous silicon (PS) layers, prepared by electrochemical etching, received widespread attention. The microstructural, chemical, electronic and opticalproperties of PS have been extensively studied by various experimental techniques. Owing to large variety of PS structures that can be produced by various techniques under different conditions, the experimental results often refer to very different PS structures. Porous silicon has many micropores and silicon residuals. The most important structural property of PS is that the single-crystalline feature of the substrate is retained even when the size or width of silicon residuals is extremely reduced during anodization. In many cases, the average diameter of crystallites is decreased down to the level of 2–3 nm. This is below a critical size for strong quantum confinement effects, since the exciton Bohr radius in silicon is 4□3 nm .
In the present work, PS samples were prepared by anodic
etching of <100> oriented *n*-type *c*-Si under illumination of light both from front and back sides for 1500, 2500, 3500, 4500 and 5500luxdillumination intensities. These samples had small Si nanocrystallites in the porous layer. They did not have considerable amount of *a*-Si, disordered Si, SiH*x* and siloxene derivatives. Si nanocrystallite size in these PS samples was obtained from Raman scattering using quantum confinement model.

II. EXPERIMENTAL DETAILS

Porous silicon samples are prepared from n-type silicon wafer of resistivity 10 ohm.cm and <100> orientation in an electrochemical system (Solartron 1280C) with the assistance of back-and front side laser illumination (He-Ne laser, 632 nm). A composition of HF (48%) and ethanol in a ration 1:1 is used for electrolyte and the anodization was carried out with constant current density (J- 10 mA/cm^2) for 30 minutes. Ethanol is often added to facilitate evacuation of H bubbles, which develop during the process.
Typical anodization arrangements are schematically shown in Figure1. The anodization is performed in current-controlled mode as it supplies the required charge for the reaction at constant rate, regardless of any evolution — during anodization — of the cell electrical impedance, ultimately leading to more homogeneous and reproducible material
In this experiment we prepared five n-type samples coded as C1,C2,C3,C4 and C5 each with constant anodization time 30min, back illumination intensity 3500lux and current density 10 mA/cm^2 at different front illumination intensities 5500, 4500, 3500, 2500 and 1500lux respectively. The front Laser source was adjusted in such a way so that the beam area is the size of the exposed surface (0.78 cm^2) of n-silicon so that the Photoinduced etching is uniform. For this we used a convex lens of exceptionally high Radius of Curvature (not measured).

After anodisation the samples were rinsed with DI water,dried and kept in vacuum chamber for three days for optical characterization using Raman- and photoluminescence (PL) spectroscopy.
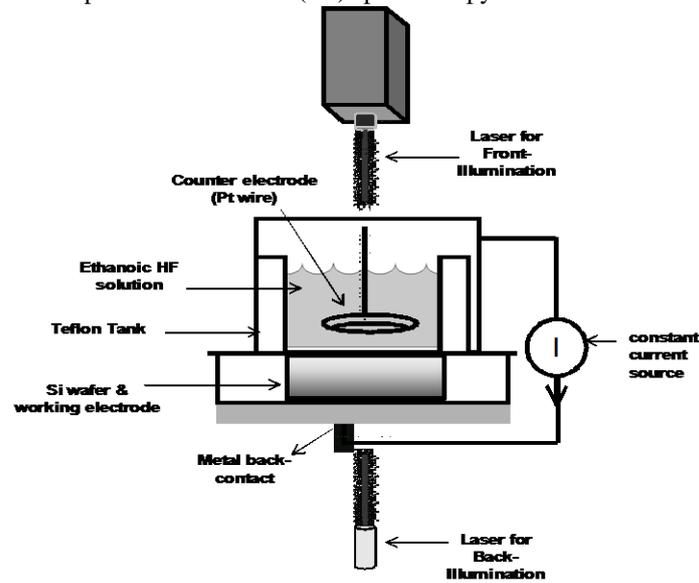

FIG.1. The Schematic drawing of the electrochemical cell used for the preparation of porous silicon of N-type samples under front and back illumination conditions
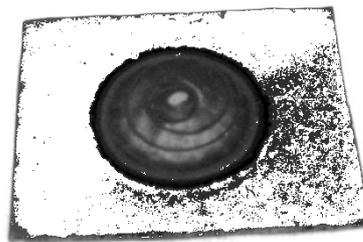

FIG.2 photograph of an N-type silicon sample of series-C after electrochemical etching.

III. RAMAN SPECTRAL STUDIES

The samples were characterized by micro-Raman spectrometer (LABRAM HR800 JY) fitted with Peltier cooled CCD detector to Study the morphology of the sample. The optical measurements were carried out at room temperature by using an air-cooled Ar+ laser with wavelength of 488nm as the excitation source. The spectrometer spectral resolution is $0.36 cm^{-1}$ at 633nm.The laser power was kept at 15mW to avoid excessive heating of the sample.

For above prepared N type P-Si samples Raman spectra was taken from the top layer and it is observed that these N-type P-Si samples have a relatively sharp (FWHM 5-10cm^{-1}) and only slightly shifted Raman signals ($\Delta w =: l$-2 cm^{-1} ', compared to bulk silicon). In the top layer, the Raman signal is only slightly shifted and narrow, and the Raman signal is equivalent to that obtained from bulk silicon .As shown in figure 3. In the top layer of our samples we notice that the shoulder at about 510cm^{-1} disappears and thus we measure a rather bulk-like Raman-signal.
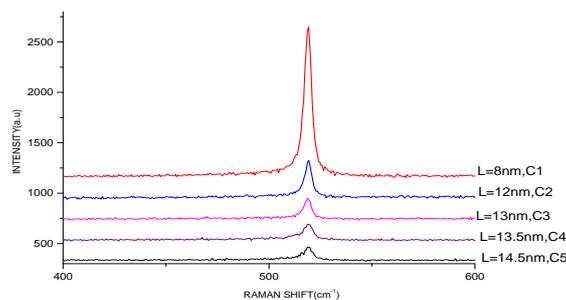

Fig. 3 Raman spectra of PS samples (N type) for different illumination intensities: (C1) 5500 LUX (C2) 4500 LUX (C3) 3500 LUX (C4) 2500 LUX (C5) 1500 LUX.

It can be seen that with increase in illumination intensity the line shape asymmetry increases but the Raman peak position does not show any shift.

Estimation of Si nanocrystallite diameter

The Raman results indicate that the P-Si Raman spectra can be used to estimate the average spherite diameter. A broadening and an increase in asymmetry of the Raman curve is observed as the illumination intensity is increased. Figure 1 showed how a Lorentzian line shape (Phonon Confinement Model) was fitted to the Raman spectrum of *c*-Si Raman spectra from LO phonon for 5, 10, 15, 20, 25 & 30min etched PS in the range from 514–520cm^{-1} . Since *c*-Si is (100) cut, LO mode is allowed and TO mode is forbidden. The fit was very good and the peak position (ω_{LO}) and the full width at half maximum (FWHM) were obtained as 520.5cm^{-1} and 5.5cm^{-1}, respectively. It is to be noted that the LO mode of PS broadens, becomes asymmetric and red shifts in comparison with that of *c*-Si. Si nanocrystallites relax the wave vector selection rule, which causes the Raman spectrum to broaden red shift and become asymmetric. Anodic etching of *c*-Si creates a nanocrystalline skeleton immersed in a network of pores. It is assumed that the Si nanocrystallites are nearly spherical in shape. In the present context, a strong phonon confinement model has been used to estimate the average diameter of the Si nanocrystallites. For spherical nanocrystallites, the first-order Raman line shape for LO phonon is given by

$$I(\omega, L) \propto \int \frac{[C(q,L)]^2 d^3 q}{[\omega - \omega(q)]^2 + [\Gamma/2]^2}$$

Where ω(q) is the phonon dispersion relation to the phonon momentum q,Γ is the natural linewidth of the bulk c-Silicon and C(q,L) is the Fourier coefficient which gives the scattering probability of phonons with different wave vector q.
The Fourier Coefficient for spherical crystallite is given by

$$[C(q,L)]^2 = \exp\left(\frac{-q^2 L^2}{4\alpha^2}\right)$$

The phonon dispersion relation ω(q) is given by

$$\omega(q) = \omega_0 - 120q^2$$

This fit did not require the necessity to include the broad Raman mode at 480cm^{-1} from amorphous silicon (*a*-Si) or the contribution from defects induced TO mode. Since the Raman intensity from the LO mode at frequencies from 460–520 cm^{-1} is quite large, the small addition of intensity around 480 cm^{-1} from *a*-Si might not be significant .

Raman spectra of several samples are shown in Fig. 3. The spectra exhibit a strong asymmetric line peaked below the bulk Si optical mode frequency of 520.0cm^{-1} that is indicative of confinement effects in c-Si. The shift down in frequency (from 520.0 cm^{-1}) and the Raman line width have been modeled for the ideal cases of spheres (dots) and rods (wires). The peak frequencies of the lines in Fig. 8 and their widths ate consistent with theoretical predictions for spheres of the diameters given in the figure. The P-Si Raman spectra can be used to estimate the average spherite diameter.

So the calculated value of crystallite size is 8, 12, 13, 13.5 and 15.5nm for C1, C2, C3, C4 and C5 respectively. So the dependence of Raman peak shift upon crystallite size obtained from Raman spectroscopy and front illumination intensity is shown in fig.4 and fig.5
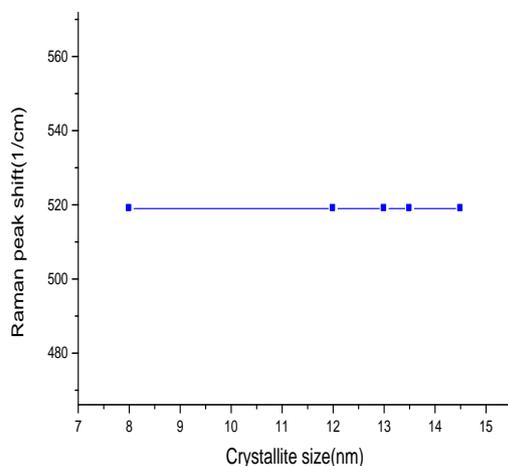

FIG.4.The dependence of Raman peak shift on crystallite size of silicon nano-crystals
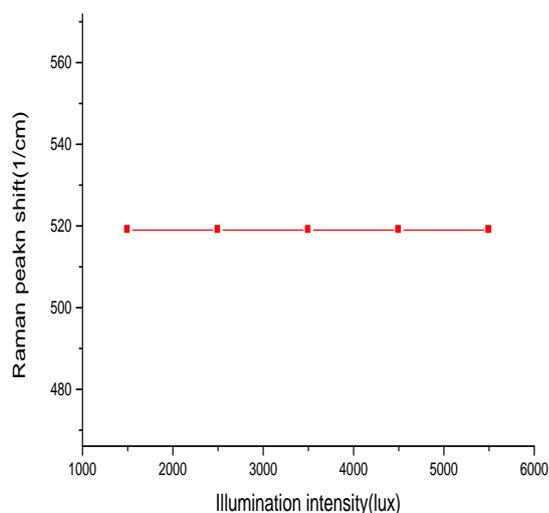
FIG.5.The dependence of Raman peak shift on front illumination intensity

It is clear from fig.4 and 5 that change in crystallite size of silicon nano crystal and illumination intensity does not show any noticeable change in Raman peak shift for our n-type samples.

IV.   PL SPECTRAL STUDIES

The photoluminescence (PL) spectra obtained for the n-type porous silicon formed using different light illumination intensities 1500, 2500, 3500 ,4500and 5500lux is shown in the Fig.6
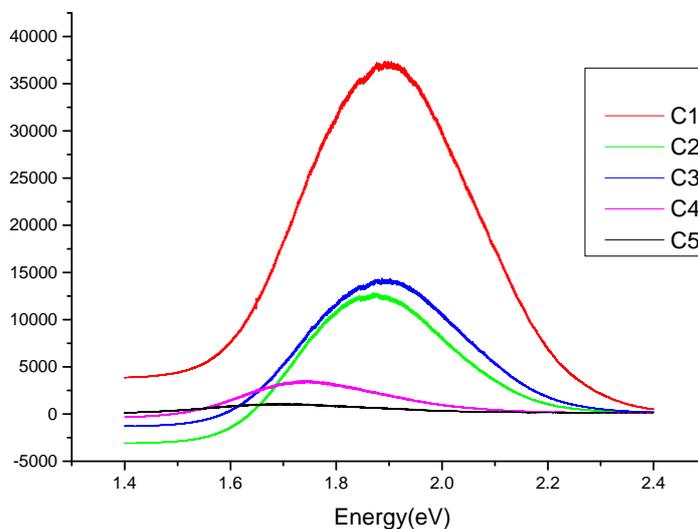

Fig. 6 PL spectra of PS samples for different illumination intensities: (C1) 5500 LUX (C2) 4500 LUX (C3) 3500 LUX (C4) 2500 LUX (C5) 1500 LUX .

Figure 6 shows the room temperature PL in the visible region that was obtained for all the light illumination level. Further it can be seen that the maximum PL intensity occurs at 1.89, 1.85, 1.84, 1.75 and 1.70eVfor the light illumination levels of 5500, 4500, 3500, 2500 and 1500lux indicating that the PL peak position has a blue shift of wavelengths as the light intensity increases. The increase of the porosity implies a decrease of the size of the crystallites constituting the layer.

It is interesting to note that the maximum PL intensity of the PS sample increases with the increasing light illumination level used and it reaches a maximum for the light illumination level of 5500lux for the n-type silicon to prepare PS. The peak energy of the PL is plotted as function of spherite size, as determined by Raman spectroscopy and illumination intensity, in fig.7 and 8.
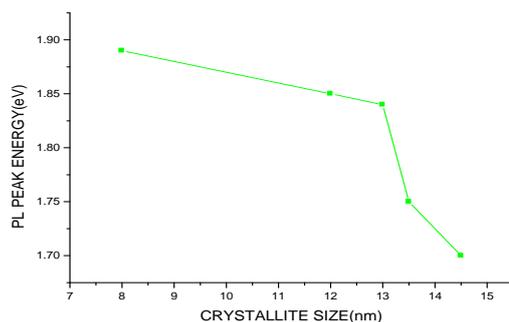

FIG.7 The dependence of PL peak energy on crystallite size of silicon nano crystals (nano particle diameter)
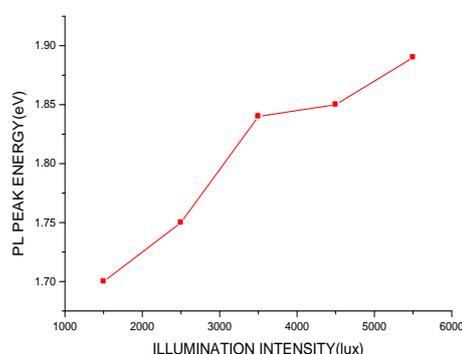

FIG.8 The dependence of PL peak energy on illumination intensity

Despite some scatter in the data, an overall increase in the peak energy with increasing confinement, decrease in crystallite size is apparent. Also increase in PL peak energy with increasing illumination intensity is observed as shown in figure8. Hence our results are relevant with Quantum confinement model. Overall increase in PL peak intensity with increase in illumination intensity is observed. It is highly likely that the increase of the PL intensity is caused by the increase in the total volume of the nanocrystallites on the surface of the PS. At the lower illumination level of 1500lux used, small pores have been formed on the silicon layer.
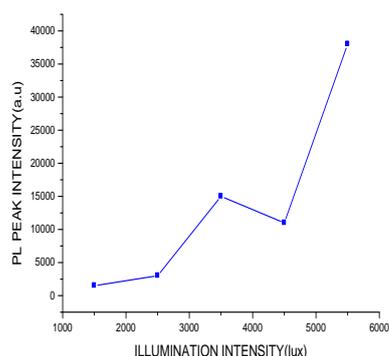

FIG.9 The dependence of PL peak intensity on illumination intensity

This is supported by a relatively low PL intensity. When the light illumination level is increased to 2500lux, there is increase in the pore diameter and correspondingly in the PL spectrum there is a good rise of the PL intensity and a blue shift of the PL peak position. When a light illumination level of 5500lux is used, the pore diameter reaches a maximum and this is reflected by maximum PL emission intensity and further blue shift in the PL peak position. So it can be concluded that as the porosity of PS increases there is increase in the blue shift of the PL peak position. Such a trend in PL peak position shifting, with increasing pore size has been reported earlier. The occurrences of room temperature PL in the visible range and the blue shift in the PL peak position with porosity of PS are strong evidences for the quantum confinement effects (QCE) in porous silicon.

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V. RESULTS AND DISCUSSIONS

The porous layer structure of N-type porous silicon samples that were fabricated by means of the electrochemical etching in 1:1 HF/Ethanol solution was studied. The dependence of the width of pores and crystallite size on etching parameters is summarized in the Table.

Table.showing the results we obtained after performing our experiment

S.NO	SAMPLE	ELECTROLYTE	ANODISATION TIME(min)	ILLUMINATION INTENSITY(lux)	RAMAN PEAK(1/cm)	PL PEAK(ev)	CRYSTALLINE SIZE(nm)
1.	C1	HF+ETHANOL	30	5800	519.26	1.89	8nm
2.	C2	HF+ETHANOL	30	4500	519.32	1.85	12nm
3.	C3	HF+ETHANOL	30	3500	519.26	1.84	13nm
4.	C4	HF+ETHANOL	30	2500	519.32	1.75	13.5nm
5.	C5	HF+ETHANOL	30	1500	519.32	1.70	14.5nm

The density of pores and width of the pores were small, when etching was performed with low illumination intensity (1500, 2500lux). In this case only a small quantity of the charge carriers was generated at the low intensity of irradiation resulting in the slow formation of rudiment in the silicon surface and slow etching of the pores. Increase of illumination intensity and concentration of charge carriers increased the silicon etching rate. so an overall increase in pore width and decrease in crystallite size with increase in illumination intensity is observed as shown in fig.10, that satisfies our previous prediction and is relevant with quantum confinement.
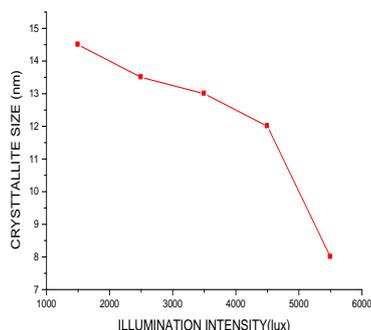

FIG.10 The dependence of crystallite size of silicon nanocrystal on illumination intensity

At low illumination intensity chemical etching prevails. Pore shape is more complex and branched. Etching anisotropy increases with the illumination intensity and contribution of electrochemical etching starts to increase. It is important to note, that at high illumination intensity (3500, 4500 and 5500lux) the depth of pores changes only slightly, but diameter of the pores is small. Fig.10 illustrates dependence of the average crystallite size versus illumination intensity. The results indicate that maximal width of pores was achieved when current density was 5500lux. That is quite higher than those find at current density 1500lux.

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